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COPPER(I) IODIDE ASSISTED REACTION OF NONACTIVATED IODOARENES WITH SODIUM TRIFLUOROACETATE IN HEXAMETHYLPHOSPHORIC TRIAMIDE. NUCLEAR TRIFLUOROMETHYLATION AND DIARYL ETHER FORMATION

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Polymethyliodobenzenes react with sodium trifluoroacetate, in the presence of copper(I) iodide, in hexamethylphosphoric triamide at 150-180°C, giving a mixture of the corresponding polymethylbenzotrifluoride, parent hydrocarbon, and bis(polymethylphenyl) ether.

Copper(I) iodide dissolves into hexamethylphosphoric triamide (HMPA) to yield a black solution which exhibits an ESR signal due to copper(II) species. In this solution iodoarenes are activated to such an extent as to undergo nucleophilic attack by thiolate,[1] selenolate,[2] tellurolate,[3] selenocyanate,[4] and azide ions.[5] We wish herein to report that nonactivated iodoarenes also react with trifluoromethyl anion *in situ* generated from trifluoroacetate by thermal decarboxylation, giving the corresponding benzotrifluorides in acceptable yields. Copper(I) promoted coupling reaction of haloarenes with sodiomalonate has recently been reported.[6]

A mixture of polymethyliodobenzene 1, sodium trifluoroacetate, CuI, and HMPA was heated under an inert atmosphere. A reaction began at around 150°C with the evolution of gaseous product. Usual work-up followed by chromatography gave comparable amounts of benzotrifluoride 2 and parent hydrocarbon 3 as the major products, and diaryl ether 4 as the minor product. The reaction failed with polymethylated chloro- and bromobenzenes. Some results are shown in the Table.

Under the same conditions, tetramethyldiiodobenzenes first suffered a reductive removal of one of iodine atoms and tetramethyliodobenzenes thus formed followed the expected course to afford 2 and 3. No bis(trifluoromethyl) derivative was obtained. Without Cu(I) salt the reaction did not take place. Similar reactions with sodium trichloro- and tribromoacetates led to a facile halogen exchange at 100 - 110°C, giving the corresponding haloarenes in high yields.

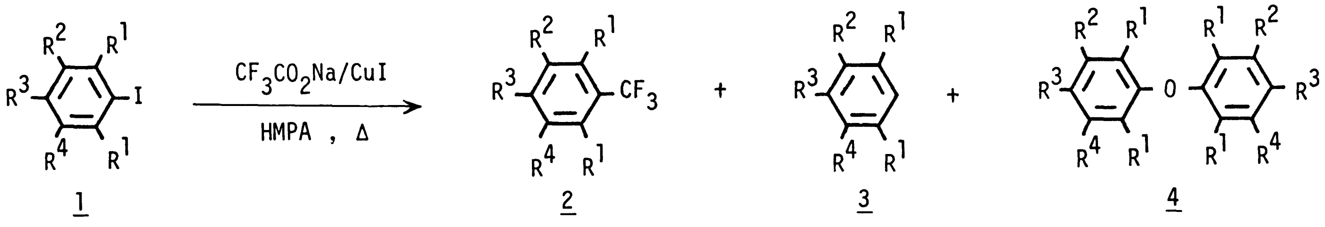

Table Products from the reaction of iodoarenes with sodium trifluoroacetate in HMPA[a]

	Iodoarene 1				Benzotrifluoride 2[b]		Hydrocarbon 3	Diaryl ether 4[b]	
	R^1	R^2	R^3	R^4	Mp (°C)	Yield (%)	Yield (%)	Mp (°C)	Yield (%)
a	Me	Me	Me	Me	101-103	38	37	191-197[c]	9
b	Me	Me	H	Me	35-37	32	36	162-163	15
c	Me	Me	Me	H	oil	38	36	134-136	13
d	Me	H	Me	H	oil	41	35	95-96	14

a Yields refer to the isolated ones and are not optimized. b Analytical and spectral data are consistent with the assigned structures. c Sublimes.

Several attempts to extend the present reaction to higher perfluoroalkanoates were unsuccessful; reactions with sodium perfluorooctanoate and ω-H-perfluoropetanoate led to the formation of fluoroalkene, hydrocarbon, and diaryl ether, no perfluoroalkylation products being obtained.

The mechanism of this trifluoromethylation has not been studied yet. However, one may expect a possible role of $CuCF_3$ and $CuOCOCF_3$ as intermediates. Alternative possibility may involve an electron transfer from Cu(I) to ArI to form $(ArI)^{\bar{\cdot}}$, which can either undergo anion-exchange to yield $(ArCF_3)^{\bar{\cdot}}$ and $(ArOCOCF_3)^{\bar{\cdot}}$, or be cleaved into $Ar^{\cdot}$ and I^-.

The reaction described here provides a new, shorter route to some polysubstituted benzotrifluorides and, in view of the time and labor required by other routes, our yields should be acceptable. A further study of this reaction, including its scope, is in progress and results will be reported elsewhere.

In a typical experiment, CuI (0.286 g; 1.5 mmol) and sodium trifluoroacetate (0.340 g; 2.5 mmol) were added to a solution of iododurene 1b (0.260 g; 1 mmol) in HMPA (3 ml) and the mixture was heated with stirring under nitrogen. The reaction began at around 150°C as seen from the liberation of gaseous product. The mixture was kept at 150-180°C for 15 h and then diluted with water, dried, and evaporated. The oily residue was chromatographed on silica gel using hexane as the eluant. Unchanged 1b, benzotrifluoride 2b, and hydrocarbon 3b were eluted in this order; Compound 2b, white plates from hexane, mp 35-37°C; yield, 65 mg (32%). Diaryl ether 4b was eluted with hexane containing ether; fine needles from ethanol, mp 162-163°C, yield, 21 mg (15%).

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